

-7N

IN-90-CR
185594
BP

FINAL TECHNICAL REPORT

Period: 1 December 1974 - 30 September 1991

Title of proposal: Theoretical molecular studies of astrophysical interest

Grant number: NSG 7105

Institution: The Trustees of Columbia University in the City of New York

Principal investigator:

George Flynn
Professor of Chemistry
Columbia University
(212) 854-4162

(NASA-CR-193300) THEORETICAL
MOLECULAR STUDIES OF ASTROPHYSICAL
INTEREST Final Technical Report, 1
Dec. 1974 - 30 Sep. 1991 (Columbia
Univ.) 13 p

N94-13781

Unclass

G3/90 0185594

When work under this grant began in 1974 there was a great need for state-to-state collisional excitation rates for interstellar molecules observed by radioastronomers. These were required to interpret observed line intensities in terms of local temperatures and densities, but, owing to lack of experimental or theoretical values, estimates then being used for this purpose ranged over several orders of magnitude. A problem of particular interest was collisional excitation of formaldehyde; Townes and Cheung had suggested that the relative size of different state-to-state rates (propensity rules) was responsible for the anomalous absorption observed for this species.

We believed that numerical molecular scattering techniques (in particular the close coupling or coupled channel method) could be used to obtain accurate results, and that these would be computationally feasible since only a few molecular rotational levels are populated at the low temperatures thought to prevail in the observed regions. Such calculations also require detailed knowledge of the intermolecular forces, but we thought that those could also be obtained with sufficient accuracy by theoretical (quantum chemical) techniques.

Others, notably Roy Gordon at Harvard, had made progress in solving the molecular scattering equations, generally using semi-empirical intermolecular potentials. Work done under this grant generalized Gordon's scattering code, and introduced the use of theoretical interaction potentials obtained by solving the molecular Schrodinger equation. Earlier work had considered only the excitation of a diatomic molecule by collisions with an atom, and we extended the formalism to include excitation of more general molecular rotors (e.g., H_2CO , NH_2 , H_2O) and also collisions of two rotors (e.g., $\text{H}_2\text{-H}_2$).

Solution of the molecular scattering equations is computationally quite expensive. As this work progressed a number of approximate molecular scattering

methods were suggested by other workers, e.g., the effective potential method of Rabitz, the coupled states approximation of Kouri and McGuire, and the decoupled l-dominant method of Alexander. As we had obtained accurate close coupling cross sections for several systems, we were in a good position to test these approximate methods. In collaboration with D. Kouri (Univ. of Houston) we also helped develop and test accuracy of the infinite order sudden approximation.

With support from this grant collisional excitation rates have now been obtained for a number of systems of astrophysical interest, including H_2 , CO, HCN, HN_2^+ , H_2CO , NH_3 , CS, OCS, HC_3N , SiO (including vibrational excitation), H_2O , CH_3CN , SO_2 , C_3H_2 , and SiC_2 . In general, work has progressed toward more complex species (i.e., with more internal degrees of freedom). Most of these calculations considered only excitation by collisions with He atoms rather than H_2 which is the dominant interstellar species. Although it has been argued that rates for excitation by these are similar, it is still important to do accurate calculations for the latter; increasing computational power should make this feasible.

It has still not been possible to obtain experimental values for the state-to-state collisional excitation rates of interest in radioastronomy. In order to obtain some check of the theoretical methods we have therefore considered other experimental data which measure related rotational relaxation phenomena. The most widely available such data (and which are also closely related to the desired rotational excitation rates) are pressure broadened linewidth parameters. We have therefore studied the theoretical calculation of line broadening cross sections. Less extensive work has also been done with NMR relaxation rates and Senftleben-Beenaaker effects. Comparison of theoretical and experimental values has generally been quite satisfactory, confirming the accuracy of the theoretical methods.

In the mid 70s and early 80s some of the most exciting work in radioastronomy

✓
9 PAGES

was the discovery of 'exotic' species in space, i.e, radicals, ions, and metastable isomers which are too reactive to have been studied in terrestrial labs. It became apparent that our expertise with quantum chemical methods could be useful in identifying some of these species. Work supported by this grant was seminal in identifying HN_2^+ , HCO_2^+ , C_3N , and C_4H in interstellar space from quantum chemical predictions of their spectral constants. In the mid 80s this grant also supported some related laboratory studies.

A number of publications have resulted from work supported by this grant, and these are listed below. Many of these publications are widely cited, both in the astrophysical and the chemical physics literature.

PUBLICATIONS resulting from research supported by NASA Grant NSG 7105

1. S. Green, "Rotational Excitation in $\text{H}_2\text{-H}_2$ Collisions: Close-Coupling Calculations", J. Chem. Phys. 62, 2271-2277 (1975).
2. S. Green, "Rotational Excitation of Molecular Ions in Interstellar Clouds", Astrophys. J. 201, 366-372 (1975).
3. S. Green, B.J. Garrison, and W.A. Lester, "Hartree-Fock and Gordon-Kim Interaction Potentials for Scattering of Closed-Shell Molecules and Atoms: ($\text{H}_2\text{CO,He}$) and (H_2,Li^+)", J. Chem. Phys. 63, 1154-1161 (1975).
4. L. Monchick and S. Green, "Validity of Central Field Approximations for Molecular Scattering: Low Energy CO-He Collisions", J. Chem. Phys. 63, 2000-2009 (1975).
5. S. Green, "Accuracy of Decoupling Approximations for Rotational Excitation: Low Energy CO-He Collisions", Chem. Phys. Letters 38, 293-296 (1976).
6. S. Green and L. Monchick, "Validity of Approximate Methods in Molecular Scattering: Thermal HCl-He Collisions", J. Chem. Phys. 63, 4198-4205 (1975).

7. B.J. Garrison, W.A. Lester, W.H. Miller, and S. Green, "Cooling of the 6 cm and 2 cm Doublets of Interstellar H_2CO by Collisions: An Accurate Quantum Mechanical Calculation", *Astrophys. J. (Letters)* 200, L175-L177 (1975).
8. S. Green and P. Thaddeus, "Rotational Excitation of Carbon Monoxide by Collisions with He, H, and H_2 under Conditions in Interstellar Clouds", *Astrophys. J.* 205, 766-785 (1976).
9. S. Green, "Rotational Excitation of Symmetric Top Molecules by Collisions with Atoms: Close Coupling, Coupled States, and Effective Potential Calculations for $\text{NH}_3\text{-He}$ ", *J. Chem. Phys.* 64, 3463-3473 (1976).
10. S. Green, "On the Accuracy of the 'Decoupled L-Dominant' Approximation for Atom-Molecule Scattering", *J. Chem. Phys.* 65, 68-70 (1976).
11. S. Green, H. Schor, P. Siegbahn, and P. Thaddeus, "Theoretical Investigation of Protonated Carbon Dioxide", *Chem. Phys.* 17, 479-485 (1976).
12. L. Monchick and S. Green, "Validity of Approximate Methods in Molecular Scattering. III. Effective Potential and Coupled States Approximations for Differential and Gas Kinetic Cross Sections", *J. Chem. Phys.* 66, 3085-3093 (1977).
13. E. Herbst, S. Green, P. Thaddeus, and W. Klemperer, "Indirect Observation of Unobservable Interstellar Molecules", *Astrophys. J.* 215, 503-510 (1977).
14. S. Green and R.N. Zare, "Ab Initio Calculation of the Spin-Rotation Constant for $^2\Pi$ Diatomics: Test of the Van Vleck Approximation", *J. Mol. Spectry.* 64, 217-222 (1977).
15. S. Green, L. Monchick, R. Goldflam, and D.J. Kouri, "Computational Tests of Angular Momentum Decoupling Approximations for Pressure Broadening Cross Sections", *J. Chem. Phys.* 66, 1409-1412 (1977).

16. S. Wilson and S. Green, "Theoretical Studies of the Butadiynyl and Cyanoethynyl Radicals: Support for the Identification of C_3N in IRC+10216", *Astrophys. J. (Letters)* 212, L87-L90 (1977).
17. R. Ramaswamy, H. Rabitz, and S. Green, "Low Temperature Rotational Relaxation in Gaseous H_2 and D_2 ", *J. Chem. Phys.* 66, 3021-3030 (1977).
18. S. Green, "Rotational Excitation in Collisions Between Two Rigid Rotors: Alternate Angular Momentum Coupling and Pressure Broadening of HCl by H_2 ", *Chem. Phys. Letters* 47, 119-122 (1977).
19. R. Goldflam, S. Green, and D.J. Kouri, "Computational Tests of the Coupled States Angular Momentum Decoupling Approximation for NMR Spin-Lattice Relaxation Cross Sections", *J. Chem. Phys.* 67, 225-228 (1977).
20. S. Green, "Comment on Fitting Ab Initio Intermolecular Potentials for Scattering Calculations", *J. Chem. Phys.* 67, 715-717 (1977).
21. S. Chapman and S. Green, "Rotational Excitation of Linear Molecules by Collisions with Atoms: Comparison of Classical and Quantum Methods", *J. Chem. Phys.* 67, 2317-2331 (1977).
22. R. Goldflam, S. Green, and D.J. Kouri, "Infinite Order Sudden Approximation for Rotational Energy Transfer in Gaseous Mixtures", *J. Chem. Phys.* 67, 4149-4161 (1977).
23. R. Goldflam, D.J. Kouri, and S. Green, "On the Factorization and Fitting of Molecular Scattering Information", *J. Chem. Phys.* 67, 5661-5675 (1977).
24. S. Green, R. Ramaswamy, and H. Rabitz, "Collisional Excitation of Interstellar Molecules: H_2 ", *Astrophys. J. (Suppl.)* 36, 483-496 (1978).
25. S. Green, B.J. Garrison, W.A. Lester, and W.H. Miller, "Collisional Excitation of Interstellar Formaldehyde", *Astrophys. J. (Suppl.)* 37, 321-341 (1978).

26. S. Green and S. Chapman, "Collisional Excitation of Interstellar Molecules: Linear Molecules CO, CS, OCS and HC₃N", *Astrophys. J. (Suppl.)* 37, 169-194 (1978).
27. T.G. Heil, S. Green, and D.J. Kouri, "The Coupled States Approximation for Scattering of Two Diatoms", *J. Chem. Phys.* 68, 2562 (1978).
28. R. Ramaswamy, H. Rabitz, and S. Green, "Rotational Inelasticity in High-Energy H₂-H₂ Collisions", *Chem. Phys.* 28, 319-329 (1978).
29. S. Green, "Computational Tests of the Infinite Order Sudden Approximation for Excitation of Linear Rigid Rotors by Collisions with Atoms", *Chem. Phys.* 31, 425-431 (1978).
30. S. Green, "On the Amount of Information in Rotational Relaxation Experiments with Application to Microwave Transient T₁ and T₂ Rates", *J. Chem. Phys.* 69, 4076-4082 (1978).
31. R. Goldflam, S. Green, D.J. Kouri, and L. Monchick, "The Effect of Molecular Anisotropy on Beam Scattering Experiments", *J. Chem. Phys.* 69, 598-605 (1978).
32. M. Guelin, S. Green, and P. Thaddeus, "Detection of the C₄H Radical towards IRC+10216", *Astrophys. J. (Letters)* 224, L27-L30 (1978).
33. H. Schor, S. Chapman, S. Green, and R.N. Zare, "Theoretical Study of Collinear Be+FH(v₁) → BeF(v₂)+H", *J. Chem. Phys.* 69, 3790-3806 (1978).
34. S. Green and E. Herbst, "Metastable Isomers: a New Class of Interstellar Molecules", *Astrophys. J.* 229, 121-131 (1979).
35. S. Green, "Rotational Excitation of Symmetric Top Molecules by Collisions with Atoms. II. Infinite Order Sudden Approximation", *J. Chem. Phys.* 70, 816-829 (1979).

36. H. Schor, S. Chapman, S. Green, and R.N. Zare, "Dynamics of the Collinear $\text{Be} + \text{FH} \rightarrow \text{BeF} + \text{H}$ Reaction", J. Phys. Chem. 83, 920-922(1979).
37. S. Green, "Vibrational Dependence of Pressure Induced Spectral Linewidths and Lineshifts: Application of the Infinite Order Sudden Scattering Approximation", J. Chem. Phys. 70, 4686-4693 (1979).
38. S. Green and D.G. Truhlar, "Rotational Excitation of Hydrogen Molecules by Collisions with Hydrogen Atoms", Astrophys. J. (Letters) 231, L101-L103 (1979).
39. S. Green, "Surprisal Analysis of Rotational-Translational Energy Transfer: Non-linear Versus Linear Rotors", Chem. Phys. 40, 1-10 (1979)
40. S. Green, "Collisional Excitation of Interstellar Molecules: Water", Astrophys. J. (Suppl.) 42, 103-141 (1980).
41. S.E. Cummins, M. Morris, and P. Thaddeus, "On C_4H Versus Vibrationally Excited CO in IRC+10216", Astrophys. J. 235, 886-888 (1980).
42. S. Green, "Theoretical Microwave Spectral Constants C_2N , C_2N^+ , and C_3H ", Astrophys. J. 240, 962 (1980).
43. S. Wilson and S. Green, "Theoretical Microwave Spectral Constants for C_3H^+ and C_4H^+ ", Astrophys. J. 240, 968 (1980).
44. S. Wilson and S. Green, "Theoretical Studies of the HeCN^+ and NeCN^+ Molecular Ions", J. Chem. Phys. 73, 419 (1980).
45. S. Green, "Energy Transfer in NH_3 -He Collisions", J. Chem. Phys. 73, 2740 (1980).
46. S. Green and L.D. Thomas, "On The Use of Pressure Broadening Data to Assess the Accuracy of CO-He Interaction Potentials", J. Chem. Phys. 73, 5391 (1980).

47. R.J. Bieniek and S. Green, "Electron Gas He-SiO Potential Hypersurface for Vibrational-Rotational Excitation through Collisions", *Chem Phys. Letters* 84, 380 (1981).
48. C.F. McKee, J.W.V. Storey, D.M. Watson and S. Green, "Far-Infrared Rotational Emission by Carbon Monoxide", *Astrophys. J.* 259, 647 (1982).
49. T.G. Heil, S. Green and A. Dalgarno, "Proton-induced Fine-structure Transitions in O IV", *Phys. Rev. A* 26, 3293 (1982).
50. R.J. Bieniek and S. Green, "Collisional Rates for Vibrational-Rotational Transitions in Circumstellar SiO Masers", *Astrophys. J. (Letters)* 265, L29 (1983).
51. S. Green, W.K. Liu, and F.R. McCourt, "Close-coupled Calculation of Viscosity Transport Relaxation for HD-He: Comparison with Experiment", *Physica* 117A, 616 (1983).
52. C.A. Gottlieb, E.W. Gottlieb, and P. Thaddeus, "Laboratory and Astronomical Measurement of the Millimeter Wave Spectrum of the Ethynyl Radical CCH", *Astrophys. J.* 264, 740 (1983).
53. C.A. Gottlieb, E.W. Gottlieb, P. Thaddeus and H. Kawamura, "Laboratory Detection of the C_3N and C_4H Radicals", *Astrophys. J.* 275, 916 (1983).
54. S.L. Davis and S. Green, "M Dependence in the Analysis of NH_3 -He Microwave Double Resonance Experiments," *J. Chem. Phys.* 78, 2170 (1983).
55. S. Chapman, M. Dupuis, and S. Green, "Theoretical Three-Dimensional Potential Energy Surface for the Reaction of Be with HF", *Chem. Phys.* 78, 93 (1983).
56. S. Green, "Metastability of Isoformyl Ions in Collisions with Helium and Hydrogen", *Astrophys. J.* 277, 900 (1984).

57. S. Chapman and S. Green, "Accuracy of the IOS approximation for highly inelastic R-T collisional energy transfer. CO-Ar", Chem. Phys. Letters 112, 436 (1984).
58. S. Green, "Calculation of pressure broadening parameters for the CO-He system at low temperatures", J. Chem. Phys. 82, 4548 (1985).
59. S. Green, "Calculation of pressure-broadened linewidths for CO in Ar", J. Quant. Spectrosc. Radiat. Transf. 33, 299 (1985).
60. S. Green, "Rotational excitation in low energy CH₃CN-He collisions", J. Phys. Chem. 89, 5289 (1985).
61. J.M. Vrtilek, C.A. Gottlieb, W.D. Langer, P. Thaddeus, and R.W. Wilson, "Laboratory and Astronomical Detection of the Deuterated Ethynyl Radical CCD", Astrophys. J. (Letters) 296, L35 (1985).
62. C.A. Gottlieb, J.M. Vrtilek, E.W. Gottlieb, P. Thaddeus, and A.Hjalmarson, "Laboratory Detection of the C₃H Radical", Astrophys. J. (Letters) 294, L55 (1985).
63. J.M. Vrtilek, P. Thaddeus, and C.A. Gottlieb, "Laboratory and Astronomical Identification of C₃H₂", Amer. Astron. Soc. Bull. 17, 568 (1985).
64. M. Broquier, A. Picard-Bersellini, B.J. Whitaker, and S. Green, "Pressure broadening cross sections for OCS-Ar, OCS-He, and OCS-H₂ collisions: a comparison between theory and experiment", J. Chem. Phys. 84, 2104 (1986).
65. S. Green, D. Cochrane, and D.G. Truhlar, "Accuracy of the energy corrected sudden scaling procedure for rotational excitation of CO by collisions with Ar", J. Chem. Phys. 84, 3865 (1986).
66. S. Green, "Collisional excitation of interstellar methyl cyanide", Astrophys. J. 309, 331 (1986).

67. S. Green, "Collisional excitation of interstellar molecules: HNC", NASA Technical Memorandum TM87791 (1986).
68. A. Palma and S. Green, "Effect of the potential well on low temperature pressure broadening in CO-He", J. Chem. Phys. 85, 1333 (1986).
69. D.C. Clary and S. Green, "Test of a modified sudden approximation for rotational excitation in He+CH₃CN", Chem. Phys. 112, 15 (1987).
70. A. Palma and S. Green, "Collisional excitation of an asymmetric rotor, silicon dicarbide", Astrophys. J. 316, 830 (1987).
71. A. Palma, "Collisional excitation of interstellar sulfur dioxide", Astrophys. J. (Suppl.) 64, 565 (1987).
72. S. Green, D.J. DeFrees, and A.D. McLean, "Collisional excitation of interstellar cyclopropenylidene", Astrophys. J. (Suppl.) 65, 175 (1987).
73. J. Boisssoles, C. Boulet, D. Robert, and S. Green, "IOS and ECS line coupling calculations for the CO-He system: influence on the vibration-rotation bandshapes", J. Chem. Phys. 87, 3436 (1987).
74. S. Green, J. Boisssoles, and C. Boulet, "Accurate collision-induced line-coupling parameters for the fundamental band of CO in He: close coupling and coupled states calculations", J. Quant. Spectrosc. and Radiat. Transf. 39, 33 (1988).
75. R. Blackmore, S. Green, and L. Monchick, "Polarized D₂ Stokes-Raman Q Branch Broadened by He: A Numerical Calculation", J. Chem. Phys. 88, 4113-4119 (1988).
76. A. Palma, S. Green, D.J. DeFrees, and A.D. McLean, "Intermolecular potential for thermal H₂O-He collisions" J. Chem. Phys. 89, 1401-1407 (1988).
77. A. Palma, S. Green, D.J. DeFrees, and A.D. McLean, "Collisional excitation of interstellar water", Astrophys. J. (Suppl.) 68, 287-318 (1988); *addendum*: 70, 681-685 (1989).

78. L.W. Avery and S. Green, "Collisional rate coefficients of C_3H_2 and the determination of physical conditions in molecular clouds", *Astrophys. J.* 337, 306–317 (1989).
79. F.C. De Lucia and S. Green, "Recent advances in pressure broadening: experiment and theory", *J. Mol. Struct.* 190, 435–446 (1988).
80. S. Green, "Effect of nuclear hyperfine structure on microwave spectral pressure broadening", *J. Chem. Phys.* 88, 7331–7336 (1988).
81. S. Green, "Pressure broadening and line coupling in bending bands of CO_2 ", *J. Chem. Phys.* 90, 3603–3614 (1989).
82. S. Green, "Collisional excitation of interstellar molecules: deuterated water, HDO", *Astrophys. J. (Suppl.)* 70, 813–832 (1989).
83. J. Boisssoles, C. Boulet, D. Robert, and S. Green, "State-to-state rotational phase coherence effect on the vibration-rotation band shape: an accurate quantum calculation for CO-He", *J. Chem. Phys.* 90, 5392–5398 (1989).
84. S. Green, R. Blackmore, and L. Monchick, "Comment on line widths and shifts in the Stokes-Raman Q-branch of D_2 in He", *J. Chem. Phys.* 91, 52–55 (1989).
85. R. Blackmore, S. Green, and L. Monchick, "Dicke narrowing of the polarized Stokes-Raman Q Branch of the $v=0-1$ transition of D_2 in He", *J. Chem. Phys.* 91, 3846–3853 (1989).
86. S. Green, "Theoretical line shapes for rotational spectra of HCl in Ar", *J. Chem. Phys.* 92, 4679–4685 (1990).
87. S. Green, "Raman Q-Branch line shapes as a test of the H_2 -Ar intermolecular potential", *J. Chem. Phys.* 93 1496–1501 (1990).
88. S. Green, Book review of *Molecular Astrophysics: a Volume Honouring Alexander Dalgarno*, edited by T. W. Hartquist, *Science* 250, 576–577 (1990).

89. S. Green, D.J. DeFrees, and A.D. McLean, "Calculations of H_2O microwave line broadening in collisions with He atoms: Sensitivity to potential energy surfaces", J. Chem. Phys. 94 1346-1359 (1991).
90. J.M. Hensley, S. Green, and G.W. Flynn, "A simple ab initio calculation for energy transfer in collisions of hot hydrogen atoms with carbon dioxide", Chem. Phys. Letters 177, 508-516 (1991).
91. S. Green, "Collisional excitation of formaldehyde in 'hot' interstellar molecular regions", Astrophys. J. (Suppl.) 76, 979-983 (1991).
92. S. Green, "Pressure broadening data as a test of a recently proposed Ar- H_2O interaction potential", J. Chem. Phys. 95, 3888-3890 (1991).
93. S. Green, "Calculation of pressure broadened spectral line shapes including collisional transfer of intensity", NATO advanced research workshop, in press.